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PRODUCTION OF FORSTERITE POWDER USING SOL-GEL TECHNOLOGY

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The effect of initial components, gel-forming additives, and heat-treatment and disaggregation conditions on the completeness of synthesis of forsterite and on powder morphology is considered. The colloid method using silica sol and magnesium acetate solution provides the steadiest and most homogeneous sol and after heat treatment yields highly dispersed powder without additional milling. The technological regimes facilitating complete synthesis are identified. Control of the synthesis temperature makes it possible to obtain powder with particle size ranging from less than 0.1 to 0.2–0.5 μm and aggregate size from 0.5 to 2–5 μm .

One of the most significant stages in the technology of new generations of ceramics is the production of initial powders. It is this stage that predetermines the shape and size of particles and aggregates dictating the choice of technological regimes and the properties of ceramics.

The use of traditional solid-phase synthesis for the production of finely dispersed nonaggregated powders is hampered mainly due to the impossibility of a uniform distribution of initial materials. To ensure a complete synthesis, it is necessary to briquette powders and apply high temperatures and long exposures. In this case strong aggregates are formed and the crystals keep growing. Subsequent milling makes the powder polyfractional and may cause its contamination by the milling bodies. Thus, the temperature at the beginning and the end of forsterite formation in a mechanical mixture of pure magnesium and silicon oxides is within the limits of 1250–1500°C. The quantity of forsterite produced at 1350°C in briquettes of magnesium oxide and quartz is 58.6% of the theoretical quantity and in briquettes of magnesium oxide and quartz glass it is 64.3% [1].

The problem of lowering the temperature of synthesis and producing highly dispersed monofractional forsterite powder with a preset size of particles and aggregates is topical considering the prospects of using forsterite single crystals [2]; therefore, special attention is paid to the chemical methods of synthesizing powders.

The methods of precipitation in a liquid phase, usually in aqueous solutions of precipitators, are widely applied. The use of the method of coprecipitation of components in an aqueous medium for the synthesis of silicates is hampered by the absence of water-soluble silicon salts, except for the silicates of alkali metals. The application of special purification methods not only complicates the process, but is frequently

ineffective, since alkali metal ions to a large extent are sorbed on the gel. Another version of this method is precipitation on a solid phase, when one of the components has no water-soluble salts. Thus, aluminum hydroxide was precipitated on the surface of highly dispersed amorphous silica in the form of Aerosil in order to synthesize mullite [3]. The distribution uniformity in this case depends on the dispersion of the solid phase and is lower than in coprecipitation. However, the technology of the synthesis of powders becomes significantly simpler and less expensive.

Modern methods of producing highly disperse powders include the sol-gel method, whose main advantages consist in producing homogeneous powders of a complex composition, lowering the temperature of synthesis, and controlling the morphology and phase composition [4]. The properties of material are determined by its composition and the method of gel production, as well as its subsequent heat treatment. There are six main variants of the sol-gel process, depending on the kind of initial materials (solutions of metal salts, soluble hydroxides, alkoxides, salt solutions combined with organic polymers, etc.), the type of the medium (water, ammonia solution), the mechanism of gel formation, etc. For instance, forsterite in [5] was synthesized by two methods: colloid and alkoxide ones. In the first case, MgO and SiO₂ sols were used for forsterite production (two-phase sol), in the second case, Mg(NO₃)₂ · 6H₂O and tetraethoxysilane (monophase sol). The x-ray phase analysis of the powders indicated that the synthesis of forsterite is fully completed at a temperature of 1100°C for the two-phase sol, whereas in using the monophase sol, forsterite formation at the specified temperature continues.

Crystalline forsterite has been obtained by the alkoxide method from tetraethoxysilane and metallic magnesium in ethylcellosolve [6]. The methods of IR spectroscopy and nuclear magnetic resonance spectroscopy identified the forma-

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TABLE 1

Sample	Initial materials	PVA additive, %	Mixing	Heat treatment	Disaggregation	Synthesis	Content of MgO, %
1	Magnesium chloride, silica sol	—	20°C, 20 min, pH = 8.2	600 and 900°C, 3 h	Dry milling, sieve No. 025	—	8*
2	Magnesium chloride, silica sol, ammonia solution	—	20°C, 60 min, pH = 9.7	The same	The same	—	6*
3	Magnesium acetate, silica sol	—	90°C, 15 min, pH = 5.4	"	"	—	14*
4	The same	30	The same	900°C, 3 h	"	—	Not determ.
5	"	—	"	900°C, 2 h	Milling in water, sieve No. 0085	1100°C, 4 h	8
6	"	15	"	The same	The same	The same	20
7	"	30	"	"	"	"	> 20
8	"	15	"	"	"	1200°C, 4 h	3
9	"	10	"	"	"	1250°C, 3 h	4
10	"	20	"	"	"	The same	3
11	Magnesium acetate, silica sol, ammonia solution	—	90°C, 15 min, pH = 9.1	"	"	"	9

* After heat treatment at 900°C.

tion of intermediate mixed magnesium and silicon cello-solvate with the Si – O – Mg link. The crystallization of the sample with forsterite formation occurs at a temperature above 680°C.

The authors of [7] proposed synthesizing forsterite from magnesium acetate solution and dispersed amorphous silica in the presence of PVA solution as the gel-forming component. According to x-ray phase analysis data, the synthesis starts at a temperature of 800°C; however, after exposure for 2 h at 1200°C it is not yet completed. Furthermore, disperse amorphous silica contains a substantial (up to 1%) amount of Na₂O, which is inadmissible for the production of single crystals.

Based on published sources and preliminary research, the present study suggests the simplest sol-gel methods that do not require complicated equipment:

- precipitation of magnesium hydroxide on amorphous silica sol particles;
- using amorphous silica sol and a solution of magnesium salt.

The choice of materials for the synthesis of forsterite was based on their availability, solubility, and decomposition temperature. Therefore, we have selected silica sol (a colloid solution of amorphous silicon oxides) and magnesium chloride and acetate. The gel-forming components tested by us were polyvinyl alcohol (PVA) and methyl cellulose.

The purpose of our study was to investigate the effect of the regimes of particular stages of the sol-gel process on the completeness of synthesis of forsterite and the morphology of powder. The completeness of synthesis was estimated based on the quantity of periclase that did not react, which was registered by means of x-ray phase analysis. The size and shapes of particles and aggregates were determined by electron-microscope analysis. In some cases a statistical

study of the distribution of aggregates by size and shape was performed.

The conditions of synthesis and the results of the diffraction phase analysis of powders are listed in Table 1. The quantities of the initial reactants were calculated for the purpose of producing forsterite of stoichiometric composition.

The main aim in using the sol-gel method was producing a steady gel by mixing magnesium chloride or acetate solution with silica sol and its transformation into gel under slow drying.

After magnesium chloride solution was poured into silica sol, its coagulation was observed. The loss of sol stability is apparently related to an abrupt change in the pH of the medium (pH of magnesium chloride solution in 5.4 and pH of silica sol is 9.5) and the compensation of the negative charge of amorphous silica particles by the adsorption of magnesium cations. Accordingly, before mixing started, the pH of magnesium chloride solution was brought up to 8 by adding ammonia solution.

The solution of magnesium acetate (temperature of 90°C) produced by dissolving magnesium oxide of grade “analytically pure” in concentrated acetic acid was slowly poured into silica sol (samples 3 – 10). PVA was dissolved in hot magnesium acetate solution or used in the form of 10% solution. After mixing for 15 min, a steady monophase sol is formed and the pH of the medium changes to 5.4. Apparently, acetate ions and also PVA molecules contribute to the stabilization of sol.

We also tested a 2% solution of methyl cellulose. However, when poured into magnesium acetate solution, it produced coagulation; therefore, the idea of using methyl cellulose was rejected.

In producing samples 2 and 11 we used the method of precipitating magnesium hydroxide onto amorphous silica

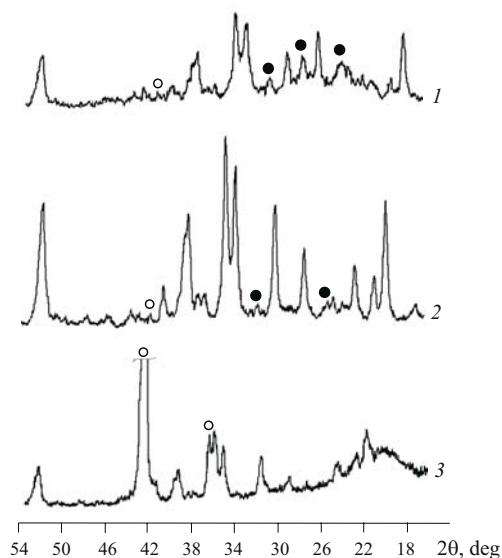


Fig. 1. Diffraction patterns of forsterite powders based on magnesium chloride (1) and magnesium hydroxide (2) after heat treatment at 600°C and based on magnesium acetate with PVA additive after heat treatment at 900°C (3): ○) periclase; ●) enstatite; without symbol) forsterite.

particles. Preliminary studies established that separating the precipitate by filtration or centrifuging disturbs stoichiometry due to the partial dissolution of magnesium hydroxide in the ammonia salt solution. Consequently, the solution of magnesium chloride or acetate was poured into a mixture of silica sol and concentrated ammonium solution. The quantity of the latter was calculated for the condition of complete precipitation of magnesium hydroxide. After mixing for 15 min, the pH of the mixture changes from 12.2 to 9.1–9.7 and either a loose precipitate (in the case of magnesium chloride) is formed, or a homogeneous suspension (in the case of magnesium acetate) that does not stratify under subsequent drying.

All resulting mixtures were dried at a temperature of 110–120°C for 20–40 h. After drying, samples 1–4 were milled in an agate mortar to passing through a No. 025 sieve (250 μm) and heat-treated at 600 and 900°C. Samples 1–4 were used to investigate the effect of the type of the initial magnesium-bearing component on forsterite formation. According to x-ray phase analysis data, the samples based on magnesium chloride heat-treated at 600°C contain forsterite, a small quantity of periclase, and a substantial amount of enstatite (Fig. 1). Furthermore, the presence of a blurred maximum (a halo) in the angle interval of 26–32° indicates the presence of an amorphous phase rich in silica. The wide bands of low intensity indicate that the process of forsterite crystallization is still at its initial stage, and the crystals contain numerous defects. The diffraction pattern of the samples obtained by the precipitation of magnesium hydroxide from a chloride solution exhibits more intense forsterite lines, whereas the amount of the amorphous phase and the enstatite is lower. This is presumably due to the lower temperature of

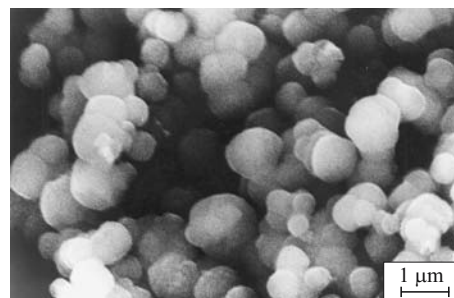
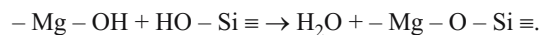


Fig. 2. Forsterite powder synthesized based on magnesium acetate.

hydroxide decomposition and, accordingly, the decreased starting temperature of forsterite formation.

After heat treatment at 900°C, the intensity of forsterite lines increases and the intensity of periclase and enstatite lines decreases. According to the data of quantitative x-ray phase analysis, the amount of periclase in the samples based on magnesium hydroxide, chloride, and acetate is equal to 6, 8, and 14%, respectively.

Thus, synthesis within the temperature interval of 600–900°C proceeds the most completely when the precipitation method is used. This is presumably related to the reaction of polycondensation of silanol groups on the surface of silica and magnesium hydroxide particles according to the following scheme:



The higher content of periclase that has not reacted in the sample based on magnesium acetate can be attributed to slower diffusion processes due to amorphous carbon that is formed in the decomposition of magnesium acetate and becomes adsorbed by the extended surface of silica particles. This carbon cannot be fully removed even after exposure for 2 h at a temperature of 900°C, which is evidenced by the gray color of the powder. This phenomenon is even more pronounced in the presence of the PVA additive in sample 4, in which forsterite formation only starts at 900°C.

To estimate the degree of dispersion and aggregation of powders synthesized at 900°C, their sintering was studied in [8]. It was established that the method of synthesis affects the apparent density of the samples before firing. The higher density values observed when magnesium chloride is used probably indicate the formation of larger and denser aggregates. Sintering in firing occurs mainly inside the aggregates; therefore, samples produced by this method have lower shrinkage.

Powders based on magnesium acetate have the most intense sintering. Thus, after firing at 1350°C the relative density of samples is 0.79 and after firing at 1600°C — 0.94. Apparently, acetate ions impede the aggregation of powder in drying and contribute to the formation of particles whose size and shape facilitate sintering. This is corroborated by the electron microscopy of the powder synthesized at 1100°C with 3 h exposure (Fig. 2). Aggregates of size 0.5–1.0 μm

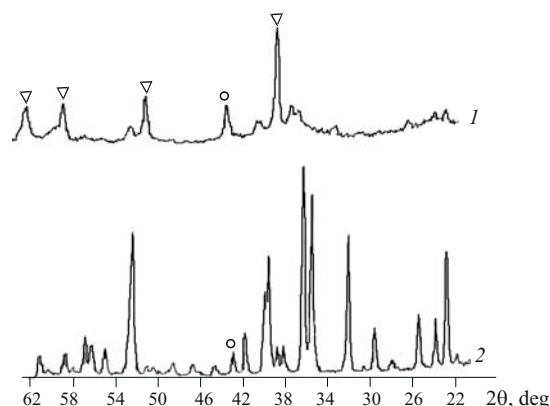


Fig. 3. Diffraction patterns of forsterite powders based on magnesium acetate after heat treatment at 900°C and milling in water (1) and after synthesis at 1250°C (2): ○) periclase; ▽) magnesium hydroxide; without symbol) forsterite.

have a rounded shape inheriting the shape of colloid silica particles.

The samples of powders obtained with 30% PVA additive after firing at 1350°C have no shrinkage and their density is lower than before firing. This loosening is presumably due to the high content of amorphous carbon in the powder synthesized at 900°C.

Thus, the sol-gel method using silica sol and concentrated magnesium acetate solution ensures the production of the steadiest and the most homogeneous sol, as well as the formation of gel under drying without adding a gel-forming agent and, after heat treatment the formation of active highly disperse forsterite powder. Furthermore, the application of these components excludes the formation of toxic compounds in heat treatment. The introduction of PVA hampers forsterite formation.

To increase the yield of forsterite, the temperature of synthesis was raised and the powder was subjected to intermediate disaggregation by milling in water. For this purpose, the powder after heat treatment at 900°C was milled for 2 h in a polyethylene drum under a ratio of forsterite balls : material : water equal to 2 : 1 : 2. The dried powder was sifted through a No. 0085 (85 μm) nylon sieve and then synthesis was performed at temperatures 1100, 1200, and 1250°C.

Milling is accompanied by the hydration of the periclase that had not reacted, which is corroborated by the data of x-ray phase analysis (Fig. 3) and can facilitate forsterite formation. Thus, the quantity of periclase in sample 5 based on magnesium acetate after synthesis at 1100°C decreases to 9% (Table 1).

The amount of periclase in samples with 10–20% PVA additive could be decreased to 3–4% only by raising the temperature of synthesis to 1200–1250°C. At this temperature, as a consequence of complete removal of residual carbon, the synthesis of forsterite is complete and the variation in the content of PVA additive within the specified interval does not affect the yield of forsterite. The quantity of

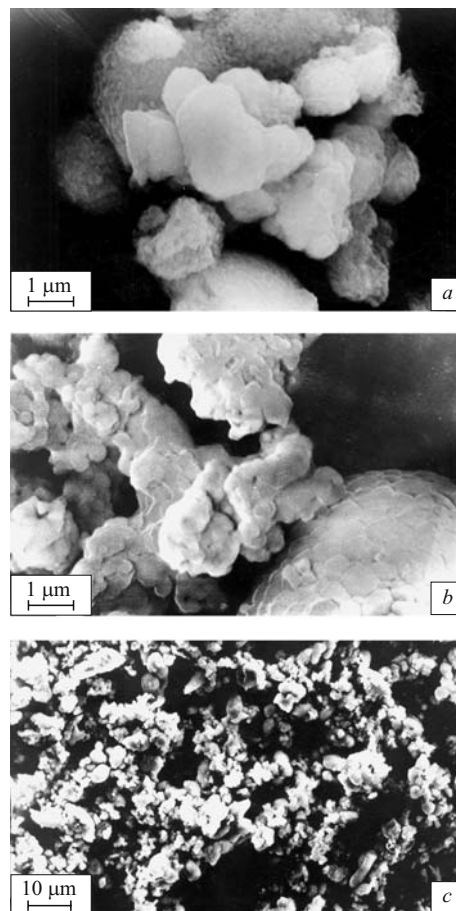


Fig. 4. Forsterite powder synthesized on the basis of magnesium acetate at temperature of 1100°C and 4 h exposure (a), at 1200°C and 4 h exposure (b), at 1250°C and 3 h exposure (c).

periclase is higher in the powder sample produced by the precipitation of magnesium hydroxide from acetate solution than from chloride solution, despite a higher temperature of synthesis.

The temperature of synthesis and the PVA additive determine not only the phase composition, but also the morphology of forsterite powder. According to electron microscopy, the size of forsterite particles after synthesis at 1100°C is less than 0.1 μm and the particles form loose isometric aggregates (Fig. 4). An increase in the temperature of synthesis to 1200°C leads to the particle size growing to 0.2–0.5 μm. At the same time, the particles acquire a clearly defined faceting due to the sintering of aggregates. Aggregates of a rounded or, more often, an irregular shape have a relief surface formed by integrating particles. Apart from the aggregates, the mixture contains single particles of size up to 1 μm.

Table 2 and Fig. 5 give examples of the electron microscope analysis of the distribution of aggregates by size and shape obtained by computerized image processing. We determined the average and maximum size of the aggregates, the shape factor as the ratio of the minimum size of the aggre-

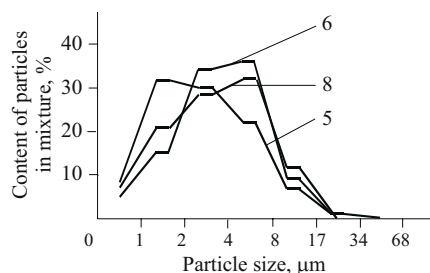


Fig. 5. Size distribution of aggregates of forsterite particles. Numbers of the curves corresponds to sample numbers.

gates to their maximum size, as well as the share of aggregates with a near-spherical shape. Samples 5, 6, and 8 have similar characteristics. The introduction of 15% PVA and raising the temperature of synthesis from 1100 to 1200°C has an insignificant effect on the size of aggregates: 90% of the aggregates do not exceed 8 μm in size, and the average size is 4.5 – 4.9 μm.

Analysis of the distribution of aggregates by shape indicates that using a gel-forming agent contributes to more spheroidized shapes. Thus, the powder synthesized at 1100°C without PVA additive has half as much spheroid aggregates as the powder with 15% PVA additive. As the synthesis temperature increases to 1200°C the quantity of spherical aggregates decreases due to their partial sintering to each other.

Powders synthesized with 10 – 20% PVA additive at a temperature of 1250°C are highly homogeneous with respect to the size of particles and aggregates. The particle size is 0.2 – 0.5 μm, and the size of aggregates with a nearly spherical shape varies from 2 to 5 μm. In contrast, powder produced by precipitation has particle size varying within wide limits: from 0.2 to 1.0 μm and the size of aggregates from 5 to 50 μm. Thus the significant variance in the size of particles and aggregates is presumably due to the highly nonequilibrium precipitation process.

To conclude, we can formulate the main conditions for producing highly disperse forsterite powder:

- use of monophase sol based on magnesium acetate solution and silica sol;
- adding 10 – 15% PVA to the sol;
- intermediate milling of the powder in water after heat treatment at 900°C;
- synthesis at 1200 – 1250°C.

The specified regimes of the sol-gel process ensure the completion of the synthesis of forsterite and the production

TABLE 2

Sample	Size* and shape of aggregates		Content of spheroid particles, %
	average, μm	averaged shape factor	
5	4.5	0.59	11
6	4.9	0.71	27
8	4.5	0.63	17

* Maximum size of aggregates in all cases is 20 μm.

of powder with a high homogeneity of size and shape of aggregates.

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